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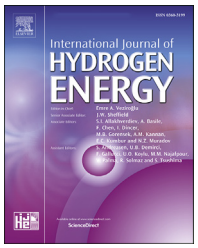

Systematic analysis of biomass derived fuels for fuel cells

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ABSTRACT

As the demand for energy continuously increases, alternatives to fossil resources must be found to both prevent fossil source depletion and decrease overall environmental impact. One solution is increasing contributions from renewable, biological feedstock, and from wastes. This paper presents an analysis of the current methods of biomass conversion, to extract biofuels and biologically produced gases to then be used in fuel cells. Pathways for converting biomass feedstock into fuel cell fuels selected here were anaerobic digestion, metabolic processing, fermentation, gasification, and supercritical water gasification, which were compared to natural gas and fossil hydrogen reference cases. These thermochemical and biological conversion pathways can also make use of residues from agriculture, forestry, or some household and industry wastes, producing hydrogen and hydrogen-rich gases. Solid oxide fuel cells were also found to be the preferred technology for such bio-derived fuel gases, due to their wide range of fuel options, wide scalability from single kW to multi 100 kW, and high efficiency.

The potential for biomass

Biomass has been utilised by human cultures for millennia and was a dominant source of energy long before the discovery of fossil fuels [1]. It is only in recent years that biomass is being re-integrated into supplying energy at a major scale. Biomass based global annual electricity production has risen from 227 TWh in 2004 to 646 TWh in 2016 [2,3]. It produces biofuels like biodiesel and ethanol, or chemical raw materials, such as for pharmaceuticals and plastics. At present, biomass is predominately used for heating in both domestic and industrial sectors, with the majority coming from traditional biomass sources, for example fuel wood. It is also used in the transport sector in the form of biofuels (0.8% of total global energy consumption, 2.8% of all transport [2]).

Lipid and protein rich agricultural crops can be employed to produce biofuels, such as biodiesel from rapeseed and palm oil, which is a versatile substitute/blender for fossil diesel. Biodiesel production increased internationally from 2.4 billion litres annually in 2004 [3] to 30.1 billion litres in 2015 [2], a factor of 12.5. However, care has to be taken that no conflicts arise between crop use for food or fuel production, causing a potential reallocation of crops from food to energy markets [4].

Abbreviations: CHP, Combined Heat and Power; LHV, Lower Heating Value; SCWG, Supercritical Water Gasification; PSA, Pressure Swing Absorption; PEFC, Polymer Electrolyte Fuel Cell; SOFC, Solid Oxide Fuel Cell; AFC, Alkaline Fuel Cell; MCFC, Molten Carbonate Fuel Cell.

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Biomass can extend to include waste streams, such as municipal solid wastes, animal wastes, and food processing wastes, or aquatic plants, including algae [5]. Biomass residues and wastes can be used as feedstock for the production of sustainable, 'carbon-neutral' hydrogen from various biopolymers like carbohydrates and lignin that are produced during the growth of biomass [5,6]. Waste biomass streams should be prioritised over using resources with existing markets. Using unutilised waste biomass decreases demands and competition for existing products, namely food, by providing new resources that can provide the same end product – gaseous or liquid energy vectors.

In the following, the term 'biomass' will be limited to wastes, embracing virtually zero costs for the feedstock, or even earning a premium by disposing of the waste agricultural slurries and waste residues, like straw, stover, and digestate, and recycled waste streams, such as forestry trimmings. Using biomass conversion pathways that yield hydrogen-rich gases like biogas and syngas (Table 1) can provide alternatives for fossil natural gas and can produce higher useable gas yields than direct hydrogen extraction for example from biohydrogen producing algae.

As biogas and syngas are rich in hydrogen content, they can be used directly (after removal of impurities) in boilers, engines, and fuel cells [e.g. combined heat and power (CHP) plants] or reformed to pure hydrogen, for use in fuel cell vehicles. Thus, a shift from fossil fuel natural gas and crude oil to hydrogen-rich gases from biological and waste sources will reduce both the demand for primary fossil resources and the amount of waste sent to landfill [12], as well as avoiding fossil CO_2 release to the atmosphere.

This study focuses on various biomass (waste) streams and investigates the sustainable potential of these biomass pathways for production of fuel gases for fuel cells [13]. It assesses production efficiencies, upgrading/reforming, and added value products. Agriculture can provide sources for biogas production from energy crops or wastes, using anaerobic digesters [14]. This technology can be used to change current aerobic digestion of wastes onsite (typically compost piles, which produce ammonia and carbon dioxide, or landfills) to anaerobic processes, which produce and capture biogas.

Systematic analysis methodology

Seven methods of biomass conversion to hydrogen-rich fuel gases were investigated via systematic literature review of the core processes, their variations (light/dark/aerobic/anaerobic), and feedstocks (summarised in Section 2). Each pathway has been summarised with inputs, outputs, and additional processes for fuel upgrading/cleaning, consolidated, and linked to their final product (biogas/(bio)hydrogen/syngas). Common biomass feedstocks for each pathway were identified from literature. Efficiency data was explored and compared against two reference cases, use of natural gas and fossil hydrogen in a fuel cell (Section 3).

Biomass paths to fuel gases

The growing interest in biomass use for energy supply has resulted in the development of many conversion techniques to produce biofuels: biological (fermentation, anaerobic digestion, and metabolic processing), thermochemical (gasification and supercritical water gasification (SCWG) for gas production, and pyrolysis and subsequent liquefaction for liquid fuels), and extraction of carbohydrates, lipids, and hydrocarbons, e.g. for alcohol and biodiesel production. Fig. 1 offers a comprehensive overview of the different pathways of turning biomass into an energy vector compatible with today's energy markets. Many of these pathways – as indicated in Fig. 1 – result in gaseous fuels that are immediately useful for operating high temperature fuel cells (including any mixtures containing hydrogen, carbon monoxide, and methane, for example) or even supply hydrogen at various purity levels. These biomass pathways and hydrogen extraction methods have been discussed in detail in Ref. [15], and have been summarised across a multitude of papers [5,15–29]. Specific reference to hydrogen and fuel gases for use in fuel cells was made in Refs. [27,30,31], also covering direct hydrogen production from algae [32]. Life Cycle Analysis of some of these production methods was covered in Refs. [33,34].

Fig. 1 demonstrates the complexity of biomass conversion, as there are many cross-overs between different pathways, for instance when unutilised (by)products from one pathway can be utilised as another's input (i.e. anaerobic digestion digestate or algal biomass for liquefaction). The flow chart is structured as per the legend, with the start of the pathways in the numbered boxes. Products throughout each stage are highlighted with thicker outlined boxes. In regards to the variety of uses these products have, the primary and secondary processes demonstrate the natural flow of where the product is currently used (primary – solid lines), and if there is an upgrading/clean-up process (secondary – dotted lines) to produce a more refined product. The alternative flows (dashed lines) show substitute applications, for instance if the bio-char produced in pyrolysis/liquefaction is not sold for revenue but is combusted (as substitute for coal) for electricity/heat generation.

Table 1 – Molar compositions of Biogas and Syngas.

Molar Composition of Biogas				Molar Composition of Syngas			
Methane	CH_4	→	~60%	Hydrogen	H_2	→	~50–52%
Carbon Dioxide	CO_2	→	~39%	Carbon Monoxide	CO	→	~25–28%
Nitrogen	N_2	→	< 1%	Carbon Dioxide	CO_2	→	~16–19%
Hydrogen Sulphide	H_2S	→	Trace amounts	Methane	CH_4	→	~4–6%
Silicon Dioxide	SiO_2	→	Trace amounts	Sulphur Dioxide	SO_2	→	Trace amounts

Adapted from Refs. [7–11].

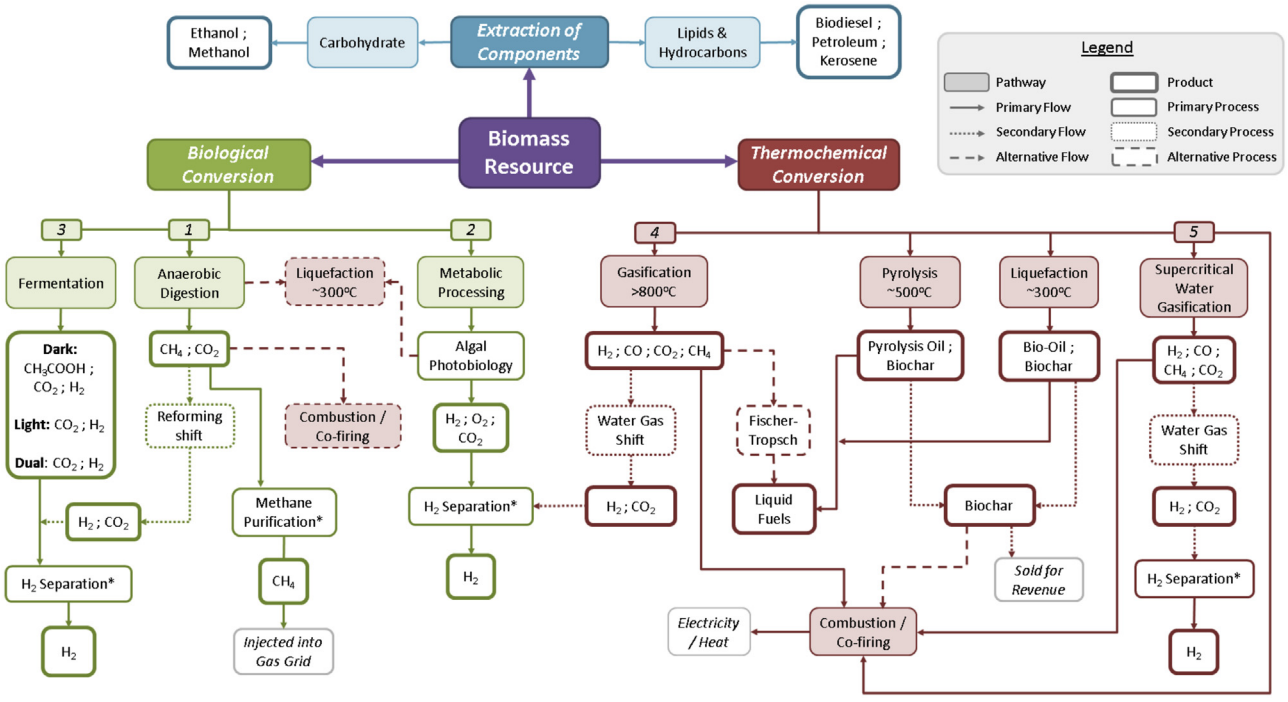

Fig. 1 – Biomass conversion pathways and biofuel extraction. *Adapted from:* [15,37].* A '*Hydrogen Separation*' or '*Methane Purification*' stage is where gas mixture components are removed to produce pure hydrogen or methane, typically via pressure swing absorption (PSA). *NB:* '*Reforming Shift*' in refers to steam methane reforming.

There are five principal pathways that produce a variety of hydrogen-rich gases from biomass. Biomass sources high in carbohydrates and proteins, such as agricultural crop wastes (*i.e.* straw and stover [35]), and waste fats and vegetable oils from food preparation [36] can be utilised by biological conversion techniques, (1) anaerobic digestion, (2) metabolic processing, and (3) fermentation, and to produce biogas, methane, and hydrogen. Alternatively, thermochemical conversion techniques, (4) gasification and (5) SCWG, utilise predominately lignocellulosic biomass (ranging from forestry residues to perennial grasses [4]) to produce syngas. Increasingly, the feedstocks are sourced from waste streams that do not impact, or are complementary to, food markets. Use of waste vegetable oils is increasing in raw materials markets, such as those for liquid fuels.

In addition, there are four pathways producing liquid fuels: Pyrolysis, Liquefaction, and Extraction of lipids/hydrocarbons and carbohydrates (un-numbered), with diesel, gasoline/petroleum, kerosene, methanol, and ethanol as an output. Liquefaction can be utilised by both thermochemical and biological conversion feedstocks, as long as the biomass has a high moisture content – such as agricultural wastes and slurries. The resulting bio-oil can be refined into liquid fuels. The final pathway is Combustion/Co-firing (not numbered), which is currently the most common method of biomass utilisation [38–44]. One of the unmentioned by-products of pyrolysis is syngas, which is not further mentioned here since it is generally used within the plant for producing process heat [45,46]. These five pathways will not be assessed as part of this paper and are only mentioned here for completeness, due to the focus being on gaseous fuels for fuel cells alone.

Pathway summary

The different pathways and their fuel gas outputs are summarised in Table 2. Natural gas and hydrogen produced from fossil sources are included as reference cases, although only the gas energy value is considered as there is no biomass input. The efficiencies of these pathways will be further evaluated in the following sections of this paper.

Pathways 2 and 3 produce hydrogen directly, and the other three have the potential to produce pure hydrogen. All pathways will require additional processes of reforming and/or purification, such as steam methane reforming, water-gas shift reaction, and/or gas separation. Alternatively, there is also dry reforming, which is a catalytic reaction where methane is reformed with carbon dioxide to produce syngas [47], much like that produced by Gasification and SCWG (pathways 4 and 5). Carbon monoxide/carbon dioxide can then be removed from the syngas via PSA to leave only hydrogen or the syngas to be processed directly in a high temperature fuel cell [48].

The nature of hydrogen production from metabolic processing should also be considered. As this process is photobiological, there is no initial input of raw biomass, only algae and what it needs to grow and produce the hydrogen alongside growth. Therefore, there are no feedstock energy values for the live algae.

Table 2 – Biological pathway feedstocks, outputs, by-products, and chemical reaction equations for various stages of conversion (references also within table).

	Pathway	Inputs	Feedstock Energy Value as received (kWh_e/kg)	Feedstock Energy Value dry and ash free (kWh_e/kg)	Outputs	By-Products	Process Stage	Process Chemical Reaction Equations	Ref's
1	**Anaerobic Digestion**	Plant Biomass Animal Slurry Biowastes	4.16	5.20	Biogas[a]	Digestate Sludge	Hydrolysis	(1) $C_6H_{10}O_4 + 2H_2O \rightarrow C_6H_{12}O_6 + H_2$	[73]
							Acidogenesis	(2) $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$	[73]
								(3) $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$	[73]
							Acetogenesis	(4) $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$	[73,74]
							Methanogenesis	(5) $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$	[73,74]
								(6) $CH_3COOH \rightarrow CH_4 + CO_2$	[73,74]
							Overall Reaction	(7) $C_6H_{12}O_6 \rightarrow 3CH_4 + 3CO_2$	[75]
2	**Metabolic Processing**	Carbon Dioxide Water Nutrients	n/a[b]	n/a[b]	Hydrogen	Oxygen Recycled Carbon Dioxide Bioreactor Sludge	*C. reinhardtii*	(8) Photons + $2H_2O \rightarrow 2H_2 + O_2$	[19,28,70,76–78]
								(9) $2H^+ + 2e- \rightarrow H_2$	[69]
							Cyanobacteria	(10) Photons + $6H_2O + 6CO_2 \rightarrow C_6H_{12}O_6 + 6O_2$	[19,28,67,70,76,79]
								(11) $C_6H_{12}O_6 + 2H_2O \rightarrow 4H_2 + 2CH_3COOH + 2CO_2$	[28,76]
								(12) Photons + $2CH_3COOH + 4H_2O \rightarrow 8H_2 + 4CO_2$	[28,76]
							ATP Phase	(13) $2H^+ + 2e^- + 4ATP \rightarrow H_2 + 4ADP + 4Pi$ (inorganic phosphate)	[69,76]
							Overall Reaction	(14) Photons + $12H_2O + \rightarrow 12H_2 + 6CO_2$	[76]
3a	**Dark Fermentation**	Biowastes Digestate Bioreactor Sludge	3.05	5.28	Hydrogen	Acetic Acid Recycled Carbon Dioxide	Heterotrophic bacteria	(15) $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$	[76]
3b	**Light Fermentation**	Biowastes Digestate Bioreactor Sludge	3.05	5.28	Hydrogen	Recycled Carbon Dioxide	Phototrophic bacteria	(16) Photons + $4H_2O + 2CH_3COOH \rightarrow 4CO_2 + 8H_2$	[65,67,76,80]
							Two stage fermentation	(17) $C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$	[65,76]
4	**Gasification**	Dry Biomass	4.36	5.78	Syngas[c]	Slag/Ash	Dry gasification	(18) Heat + $2C_6H_{10}O_5 + 4H_2O \rightarrow 10H_2 + 6CO + 4CO_2 + 2CH_4$	[1,92]
							Water-gas shift reaction	(19) $6CO + 6H_2O \rightarrow 6CO_2 + 6H_2$	[28]
5	**Supercritical Water Gasification**	Wet Biomass Water	4.36	1.94[d]	Syngas[c]		Wet gasification	(20) Heat + $2C_6H_{10}O_5 + 5H_2O \rightarrow 13H_2 + 7CO + 4CO_2 + CH_4$	[11,93]
							Water-gas shift reaction	(21) $7CO + 7H_2O \rightarrow 7CO_2 + 7H_2$	[28]
RCa	***Reference Case NG***	*Sour Natural Gas*[e]	*n/a*[f]	*n/a*[f]	*De-sulphured Natural Gas*	*Contaminant Gases (Sulphur)*	*Desulphurisation*	*(22) [$CH_4 + C_2H_6 + N_2 + CO_2 + SO_2$] + AC (Activated Carbon) → [$CH_4 + C_2H_6 + N_2 + CO_2$] + [$SO_2$ + AC]*	[94,95]
RCb	***Reference Case H2***	*Sour Natural Gas*	*n/a*[f]	*n/a*[f]	*(Fossil) Hydrogen*	*Carbon Dioxide (and Sulphur)*	*Steam reforming*	*(23)* $CH_4 + 2H_2O \rightarrow 4H_2 + CO_2$	[18]

Background sources: Anaerobic Digestion – [49–55], Metabolic Processing – [56–64], Fermentation – [28,65–72]Background sources: Gasification – [12,81–84], SCWG – [8,84–87], RC Natural Gas – [88], RC Hydrogen – [21,89–91].
Assumed chemical compositions, equations, and feedstock energy values from literature and Phyllis2 [7–11,93,94,96].

[a] Biogas composition (~60% CH_4, ~39% CO_2, ~1% N_2, trace H_2S).
[b] Metabolic processing has no raw biomass input (photobiological process).
[c] Syngas composition (~50–52% H_2, ~25–28% CO, ~16–19% CO_2, ~4–6% CH_4, trace SO_2).
[d] SCWG biomass is processed by increasing the moisture content, not reducing it via drying.
[e] Sour Natural Gas composition (~95% CH_4, ~2.5% C_2H_6, ~1.5% N_2, <1% CO_2, trace SO_2).
[f] Sour Natural Gas has no feedstock as there is no biomass input.

Fuels for fuel cells

Fuel cells use a variety of fuels, typically hydrogen, to produce electricity, water, and heat [97] with air typically being the oxidant. They are modular units, built in a variety of sizes and types, but the principal behind each of them is the same [97]: a fuel cell is made up of a fuel electrode with an oxidation catalyst (anode), and an air electrode with the oxygen reduction catalyst (cathode), both sides separated by the electrolyte 'membrane'. For this paper, one fuel cell from each end of the temperature spectrum will be assessed for generation of 1 MWh of electrical output, using gases produced from the summarised biomass conversion pathways.

Fuel cell electrochemical processes occur on the electrode-membrane interface (triple phase boundary). Output is therefore dominated by the total surface available for reactions. To increase the output of the fuel cell, the accessible surface area of the electrodes must increase, both by increasing the overall geometric size as well as the catalyst surface (e.g. introducing nanoparticles). The catalysts within the anode and cathode adsorb and electrochemically split the fuel and oxygen molecules, sending electrons to an external circuit, thus producing an electrical current. The ionised species produced pass through the membrane, taking up the electrons on the opposite electrode. In the hydrogen fuel case, this solely produces water, being removed from the fuel cell as water vapour.

The fuel cell spectrum: a brief overview

This study compares the different biomass conversion systems and the fuels they produce and combines them with different fuel cell applications. There are many different types of fuel cells that could be explored in the latter half of this work. Fig. 2 illustrates the temperature ranges of the different fuel cells and their ionic charge carriers, assuming hydrogen fuel. The fuel cells operating at the lowest and highest temperatures (Polymer Electrolyte Fuel Cell (PEFC) and Solid Oxide Fuel Cell (SOFC)) are the chosen technologies for assessment in this paper. This is not just due to their operating conditions, but also because they are the most commercially available fuel cells and demonstrate both the narrowest and widest use of gaseous fuels. Other fuel cell types include Alkaline (AFC), Phosphoric Acid (PAFC), and Molten Carbonate (MCFC) Fuel Cells [98], and advancements are being made in bio-fuel cells (made with bio-electrocatalysts made from microorganisms [99].

Solid Oxide Fuel Cell

This is a ceramic fuel cell that has a high temperature and a lower temperature variation. It has a solid ceramic electrolyte, non-platinum catalyst [104], and operates on inputs of, amongst others: syngas, natural gas, biogas, methane, or hydrogen at ~650–800 °C [30,100]. Logically, if the fuel gas contains carbon, the fuel cell will emit carbon dioxide. This emission is carbon-neutral if the fuel gas has been sourced from biomass. Therefore, net carbon emissions only result from using fossil resources such as town gas or natural gas, both in the fuel stream itself and any ancillary energy consuming steps involved in processing the fuel gas, which are driven by fossil sources.

Low temperature variations of SOFCs run at 500–600 °C [105]. They lose the potential of internal reforming and will need to be operated on hydrogen or syngas [103]. SOFCs are currently predominately used for CHP in domestic and industrial applications [106,107], as well as auxiliary power units on vehicles [30,108].

Polymer Electrolyte Fuel Cell

This is one of the most employed low temperature fuel cells, due to its compact size and relative high volumetric and gravimetric output capacity. Polymer electrolyte fuel cells (PEFC) have a solid polymer membrane electrolyte and a platinum catalyst, which is susceptible to carbon monoxide contamination [101]. Due to this, PEFCs can only use pure hydrogen to produce electricity, heat, and water at ~80 °C [100]. PEFC are predominately employed in mobile applications such as most all current fuel cell vehicles [109,110], but also in uninterruptible power supply units, as well as stationary applications in domestic and industrial environments [111,112].

Pathway comparison

The five pathways analysed in Table 2 convert biomass using different methods to yield a variety of fuel gas products. Most of these fuels can be utilised in the different fuel cell technologies explored in Section 3.1, some of which have internal reforming, such as SOFCs [30], but gases may require cleaning up to prevent, for example, sulphur poisoning [30]. This is due to catalysts, such as platinum or nickel, being very sensitive to impurities including sulphur, particulate matter, corrosive components such as chlorine or fluorine, and siloxanes (oxidises into silicon dioxide), which will compromise the performance and efficiency of the fuel cell.

In Table 3, chosen pathway outputs, fuel gas clean-up/reforming processes, fuel gas lower heating values (LHVs), and the potential fuel cell applications have been summarised.

Fuels with high energy content, such as hydrogen, are predominately the result of additional processing. However, it is also directly produced in two biological processes, metabolic conversion, and light/dark fermentation. Nevertheless, both of these pathways initially have low efficiencies, due to the (photo)biological limitations of the micro-organisms involved [119]. The pathway efficiencies for gas production, clean-up/reforming processes, and use of fuel gases have been calculated below. Fig. 3 demonstrates how the whole system works together, with products undergoing four stages of conversion: *Stage 1* – raw biomass to useable 'chemical' feedstock, *Stage 2* – feedstock to raw gas, *Stage 3* - raw gas to fuel gas, and *Stage 4* – fuel gas to electrical output.

These stages were calculated in reverse order, owing to the choice of 1 MWh of electrical fuel cell output as the functional unit. The amount of biomass feedstock and fuel gas was required at each stage was calculated starting from *Stage 4* and working backwards, based on available data and background research (Equations (24)–(30)).

For *Stage 4*, the specific 'fuel cell output' (FCO) required to produce a functional unit of 1 MWh electrical output was

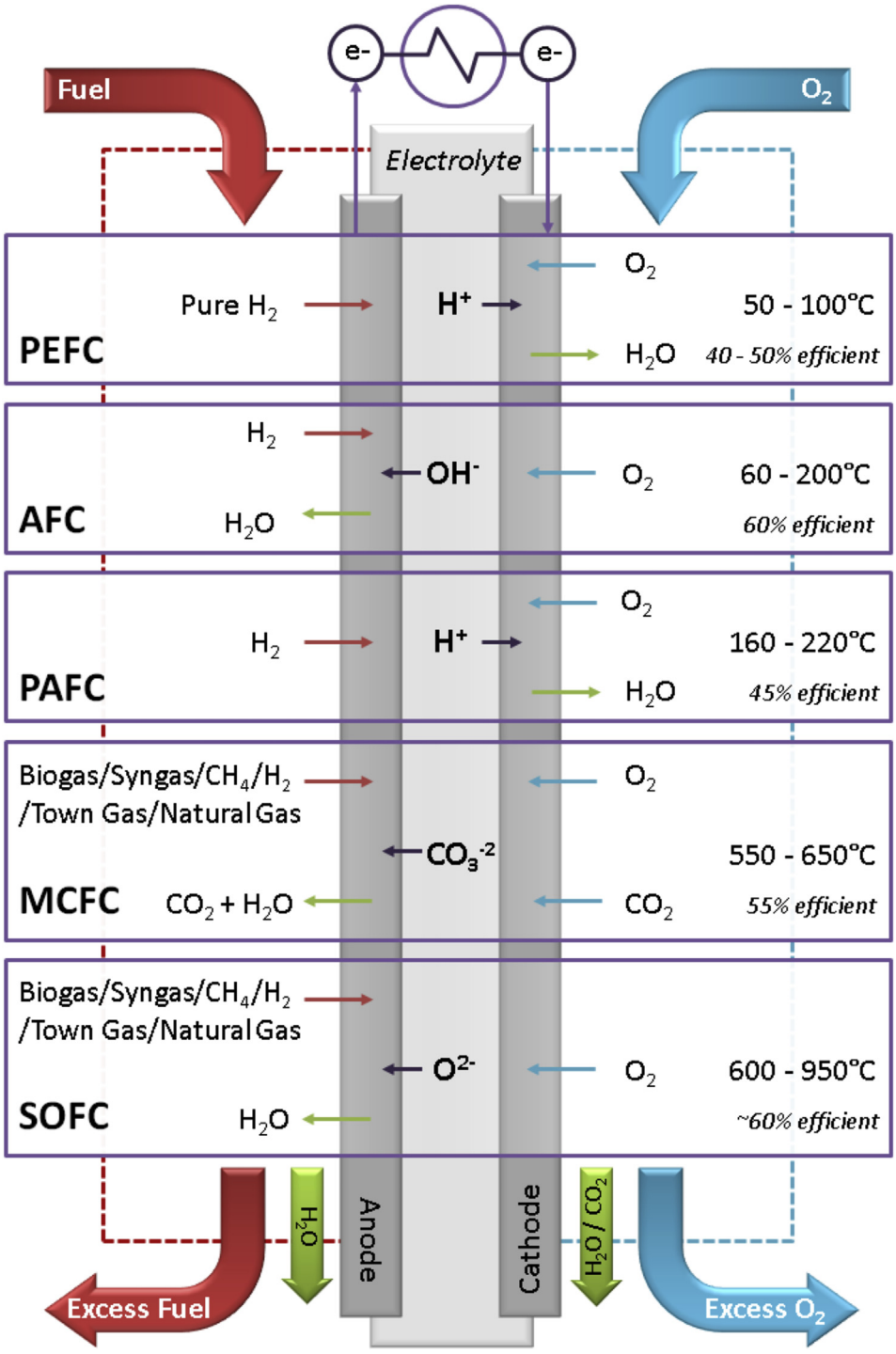

Fig. 2 – Overview of fuel cell technologies, fuel inputs, outputs, operating temperatures, and efficiencies. ***Data and Diagram modified from:*** **[97,100–103]. Notes: (a) AFC efficiency relates to operation on pure oxygen, the others to use of air (21% oxygen). (b) MCFC can only operate on hydrogen if a separate carbon dioxide feed is provided to the cathode.**

Table 3 – Biomass conversion pathways, produced fuel gases, and potential fuel cell applications. Separation and purification sources [113–118].

	Pathway	Outputs	Possible Gas Clean-up/Reforming Process(es)	Fuel Gas	Fuel LHV (kWh_e/kg)	Fuel Cell Applications
1	**Anaerobic Digestion**	Biogas	H_2S & SiO_2 removal via pressure swing absorption (PSA) CO_2, N_2, SO_2 & SiO_2 removal via PSA.	Biogas. Biomethane.	10.00 13.89	SOFC, MCFC. SOFC, MCFC.
			Steam reformed biomethane/water-gas shift (WGS) and purification.	Hydrogen (BM).	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
2	**Metabolic Processing**	Hydrogen	Separation from O_2 and recycled CO_2 via PSA.	Hydrogen.	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
3a	**Dark Fermentation**	Hydrogen	Separation from O_2 and recycled CO_2 via PSA.	Hydrogen.	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
3b	**Light Fermentation**	Hydrogen	Separation from O_2 and recycled CO_2 via PSA.	Hydrogen.	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.
4	**Gasification**	Syngas	Removal of particulates and corrosive components (SO_2). WGS and separation.	Syngas. Hydrogen (SG)	3.61 33.34	SOFC, MCFC. SOFC, (MCFC*), PAFC, AFC, PEFC.
5	**Supercritical Water Gasification**	Syngas	Removal of particulates and corrosive components (SO_2). WGS and separation.	Syngas. Hydrogen (SG).	3.61 33.34	SOFC, MCFC. SOFC, (MCFC*), PAFC, AFC, PEFC.
RCa	*Reference Case Natural Gas (NG)*	*De-sulphured Natural Gas*	*Absorption separation process to remove sulphur.*	*De-sulphurised Natural Gas.*	13.89	SOFC, MCFC.
RCb	*Reference Case H_2*	*(Fossil) Hydrogen*	*Steam reformed natural gas/WGS and purification.*	*(Fossil) Hydrogen.*	33.34	SOFC, (MCFC*), PAFC, AFC, PEFC.

Gas compositions as in Table 1; (*) allowing for additional carbon dioxide feed to the cathode.

calculated as shown in Equation (24). The FCO was then used to determine the 'fuel gas demand' (FGD) for this 1 MWh system, using Equation (25) to convert from kWh to MWh.

$$FCO\ (kWh_e/kg) = LHV * FCE \quad (24)$$

$$FGD\ (kg) = 1000 / FCO \quad (25)$$

The 'raw gas demand' (RGD) was calculated for *Stage* 3 to determine how many kg of unprocessed raw gas are produced per MWh of feedstock (Equation (26)). This used the fuel gas demand (FGD) and (if any) 'clean-up/reforming process efficiencies' (CRPE) for refined fuels. For CRPE of PEFC fuel gases, only the purification via PSA process applies, as SOFCs conversely have (internal) reforming processes already included in the fuel cell efficiency itself. If there is more than one clean-up/reforming step, Equation (27) is implemented as part of Equation (26), with the mol ^{wt}% only being applied when separating specific gas from a mixed fuel, i.e. ^{wt}% of methane content within biogas for extraction and clean-up.

$$RGD\ (kg/MWh) = FGD\ (/\ CRPE)\ \text{if applicable} \quad (26)$$

$$CRPE\ (\%) = Eff._1 * Eff._2\ (* \text{mol } {}^{wt}\%)\ \text{if applicable} \quad (27)$$

To make this assessment complete, the total feedstock involved in the pathway was also required, so that lower efficiency pathways were better represented. The 'chemical feedstock demand' (CFD) was calculated for *Stage* 2 (Equation (28)), using the RGD divided by the pathway's 'conversion process efficiency' (CPE). This corresponds to the chemical conversion reactions (glucose/cellulose *etc.*) within the raw waste biomass, which varies with each pathway.

$$CFD\ (kg/MWh) = RGD / CPE \quad (28)$$

The overall equation for calculating FGD from CFD is shown in Equation (29):

$$FGD\ (kg/MWh) = CFD * CPE * CRPE \quad (29)$$

Once the CFD has been calculated, the calculation for *Stage* 1 can be made to determine the amount of raw feedstock demand (RFD) required. It is assumed that any raw feedstock received will go through refinement processing first (drying, sorting, homogenising *etc.*); we will only refer to the useful components in wet and dry condition (as received feedstock, F^{ar}). For further calculation of conversion stages, we consider the dry and ash free feedstock (F^{daf}) as the pure chemical fuel component stripped of any inorganic matter. As a technical process this is not be completely accurate since an 'ash removal' will normally take place within the conversion process, e.g. as the ash from combustion or sand deposits in fermentation. Nevertheless, in the physio-chemical processes involved, only the chemical energy content (enthalpy, HV) of the feedstock will be converted, thus effectively referring to the convertible substance fraction alone (i.e. in F^{ar}). We therefore use this concept in back-tracing the total amount of feedstock required since online biomass databases, such as Phyllis [96], provide LHV data for the two categories F^{daf} and

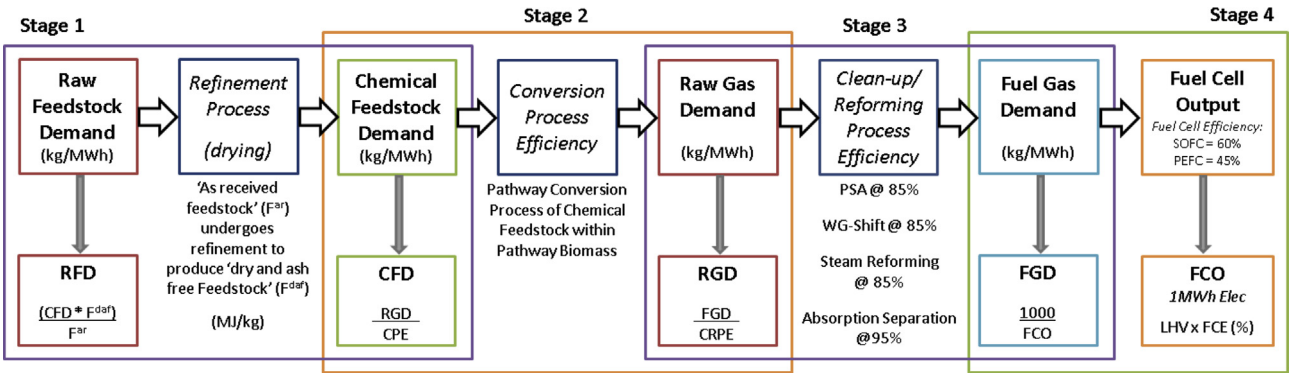

Fig. 3 – Raw biomass feedstock to fuel gas process chain.

F^{ar}. By using these two values, the CFD can be converted to RFD, as in *Equation (30)*, by transforming between units of kg and MJ.

$$(\text{CFD (kg/MWh)} * F^{daf} \text{ (MJ/kg)}) / F^{ar} \text{ (MJ/kg)} = \text{RFD (kg/MWh)} \quad (30)$$

It is with this RFD unit that we can determine how much original feedstock is required per MWh of electrical output from the produced gaseous fuel, thus offering an assessment of the overall efficiency of the process chain and the effort in supplying the feedstock.

Fuel cell fuels analysis

All biological pathways discussed above can provide fuels for the fuel cell technologies discussed in this paper. This is because metabolic processing and fermentation directly produce hydrogen, with the advantage of being able to use waste feedstocks. Conversely, thermochemical pathways predominately produce fuels for high temperature fuel cells, at a high efficiency, with reforming options for producing hydrogen for the low temperature fuel cells. The most commonly used fuel cells at the time are SOFC for high temperature and PEFC for low temperature, and so these were used for further analysis, displayed in Table 4. The pathway efficiencies shown are the initial conversion efficiencies for the chemical compositions of the biomass feedstocks found across literature. These efficiencies, as explained above, apply purely for the convertible part of the biomass.

Anaerobic digestion and gasification efficiencies are 75% [120–123]; for SCWG the value is taken as 70% [124,125]. The clean-up and reforming efficiencies are representative for the convertible gases (biomethane/natural gas) with 85% efficiency [91,126]. This is also true for syngas carbon monoxide upgrading to hydrogen using a water-gas shift reaction, with 85% efficiency [127]. Research has been conducted with catalyst membranes, potentially increasing WGS efficiency up to 95% [128,129]. 1 kg of Biomethane is produced from 1.15 kg biogas (87%). Hydrogen produced from biomethane and syngas requires an additional purification process with 85% efficiency before entering the (low temperature) fuel cell.

The biological hydrogen pathways are slightly different, as their efficiencies are determined by the biological limitations of the organisms driving the reaction. The algae producing hydrogen via metabolic processing have a maximum production efficiency of 10% [119,130]. Dark and light fermentation bacteria have a low biological conversion (15% and 10%, respectively [19]) but a high hydrolysis conversion efficiency of 50% and 80% [65]. This results in pathway efficiencies of 9% and 6%. The clean-up efficiencies for these pathways are 85%, reflecting an 80–90% PSA efficiency [131,132].

For the natural gas and fossil hydrogen reference cases, there are no initial process efficiencies as extraction of natural gas from a reserve, which is estimated at 60–80% [133], is not comparable to extraction of gases from biomass. Therefore, it has been omitted and grid natural gas has been selected. From there, the absorption separation membrane uses activated charcoal to produce de-sulphurised natural gas with 95% efficiency [134]. This natural gas can also produce (fossil) hydrogen via steam reforming at 85% efficiency, in addition to the 95% efficiency of the natural gas clean-up, and the 85% efficient purification process.

A first inspection of Table 4 shows that SOFCs are more efficient in converting biomass-derived fuels than PEFC, due to their higher performance and greater variation of fuels (Fig. 2, previous). Of these 19 pathways (twelve SOFC vs. seven PEFC), Table 4 initially found anaerobic digestion biogas and gasification syngas to be the most efficient pathways at 75%.

The fuel cell output represents the amount of electrical output (kWh_e) possible from 1 kg of fuel gas. The fuel gas demand denotes the quantity of fuel gas required to deliver the 1 MWh fuel cell electrical output functional unit. Equation (25) demonstrates how the data is converted from kWh to MWh. Ideally, the lower the quantity of fuel gas required to achieve the 1 MWh functional unit, the more sustainable its performance. Seven of the twelve SOFC fuels achieved the lowest quantities, at 50kg/MWh, due to the high electrical efficiency and the high gravimetric energy density of hydrogen fuel. Six of the seven PEFC fuels used 66kg/MWh due to the lower FUE. All seven SOFC fuels had fuel gas demands below 100kg/MWh; the other five were up to 500 kg. Unfortunately, the amount of fuel gas alone does not allow any estimates of sustainability of the specific pathway. The key factors here are the electrical efficiency of the fuel cell and the high gravimetric energy density of hydrogen fuel.

However, some pathways produce higher gas yields per kg of feedstock than others, so to allow for this, the feedstock demand for each pathway's fuel gas demand was calculated.

Table 4 – Full biomass and reference case pathways, their fuels, and efficiencies for SOFC and PEFC *Data modified from:* [18,19,65,93,96,119–125,128–132,135–143].

	Pathway	Process Efficiency	Gas Clean-up /Reforming Efficiency	Fuel Gas	Fuel LHV ($kWh_{eq.}/kg$)	Fuel Cell Efficiency	Stack Fuel Demand (kg/MWh)	Chemical Feedstock Demand (kg/MWh)	Feedstock Energy Values *As received* ($kWh_{eq.}/kg$)	*Dry & ash free* ($kWh_{eq.}/kg$)	Raw Feedstock Demand (kg/MWh)
1a	**Anaerobic Digestion**	75%	n/a	Biogas. Biomethane	10.00	SOFC ~60%	166.65	261.42	4.16	n/a	261.42
1b			85%	Hydrogen (BM)	13.89	SOFC ~60%	119.99	267.62	4.16	n/a	267.62
1c			85% * 85%		33.34	SOFC ~60%	49.99	655.86	4.16	n/a	655.86
						PEFC ~45%	66.66	874.58	4.16	n/a	874.58
2	**Metabolic Processing**	10%	85%	Hydrogen	33.34	SOFC ~60%	49.99	n/a	n/a	n/a	588.19
						PEFC ~45%	66.66	n/a	n/a	n/a	784.25
3a	**Dark Fermentation**	9%	85%	Hydrogen	33.34	SOFC ~60%	49.99	653.46	3.05	5.29	1131.66
						PEFC ~45%	66.66	871.38	3.05	5.29	1508.88
3b	**Light Fermentation**	6%	85%	Hydrogen	33.34	SOFC ~60%	49.99	1069.30	3.05	5.29	1851.80
						PEFC ~45%	66.66	1425.91	3.05	5.29	2469.07
4a	**Gasification**	65%	n/a	Syngas.	3.61	SOFC ~60%	461.50	723.92	4.36	5.78	960.62
4b			85% * 85%	Hydrogen (SG)	33.34	SOFC ~60%	49.99	1053.01	4.36	5.78	1397.30
						PEFC ~45%	66.66	1651.98	4.36	5.78	2192.11
5a	**Supercritical Water Gasification**	70%	n/a	Syngas	3.61	SOFC ~60%	461.50	775.63	4.36	n/a	775.63
5b			85% * 85%	Hydrogen (SG)	33.34	SOFC ~60%	49.99	1128.23	4.36	n/a	1128.23
						PEFC ~45%	66.66	1504.48	4.36	n/a	1504.48
RCa	***Reference Case Natural Gas***	*85%*	*95%*	*De-sulphurised Natural Gas*	*13.89*	*SOFC ~60%*	*119.99*	*166.29*	*n/a*	*n/a*	*166.29*
RCb	***Reference Case Fossil Hydrogen***	*85%*	*85% * 85%*	*(Fossil) Hydrogen*	33.34	SOFC ~60%	49.99	325.83	*n/a*	*n/a*	386.92
						PEFC ~45%	66.66	434.29	*n/a*	*n/a*	515.95

These were established based on the reaction equations explored in Section 2, as well as literature data. This was predominately due to the varieties of different reactor types, capacities, outputs, and feedstock LHVs, which will be discussed in Section 3.3.

Of the biological pathways, algae perform biological metabolic processing, which directly uses photons from light to produce energy for breaking down water. The solar conversion efficiency is very low due to their biological limitations (<10%) [130]. Light fermentation bacteria also have these constraints. Some bacteria that are used in dark fermentation cannot produce hydrogen directly due to thermodynamic constraints [19]; some bacteria cope with this by producing methane first, which they can then break down into carbon dioxide and hydrogen. This inhibition decreases their biological performance down to <15% conversion efficiency [19,67].

In addition, both fermentation pathways have a wide range of substrate hydrolysis efficiencies *i.e.* consumption of feedstock (30–40% up to 80–95%) depending on the composition of the feedstock [28,65]. Algal bioreactor sludge was utilised as a feedstock, which has an estimated 65% (±15%) substrate hydrolysis efficiency for dark fermentation and 55% (±10%) for light fermentation [65]. When simplified to include both biological limitations and substrate efficiencies, the pathway efficiencies for dark and light fermentation are estimated to be 9% and 6%, respectively.

Due to the feedstock demand having the highest level of influence, the above findings have the potential to reorder the performance ranking across the 19 pathways.

Key findings

The fuel gas pathways and fuel cell combinations were highlighted based on best performances across four parameters: fuel cell output, fuel gas demands, raw gas demands, and raw feedstock demands. These affect each pathway's performance for producing a 1 MWh of fuel cell electrical output and have been ranked in order of lowest to highest feedstock use (Table 5). This ranking attempts to reflect the efficiency of the process chain to produce a given amount of electricity by inspecting the amount of feedstock necessary. This amount not only indicates the quantity of feedstock, but also hints at transport energy requirements. In interpreting this table, though, care must be given to the quality of the feedstock. A lower quality feedstock (e.g. sewage sludge) may imply higher mass, but might be preferable to lower amounts of higher value feedstock (e.g. waste fats) that could be to alternative uses. This aspect, though, has not been fully investigated in this paper. Nevertheless, Table 5 gives first indications of feedstock quality.

Out of the biological pathways, anaerobic digestion biogas and biomethane had the lowest feedstock demands, fuel gas demands, and highest fuel cell output, with the fossil hydrogen reference cases both above and below, demonstrating the potential of anaerobic digestion potential as a competitive processing method. It is understood that using gas-grid reference cases does not result in fully comparable values, but by comparing the performance of existing pathways to that of alternative pathways, it is possible to scale the process chains against the reference cases. All four top ranking pathways have results for SOFC systems. Both fermentation pathways showed the most promising performance, in regards to high fuel cell output and low fuel gas demand, but have the highest feedstock demands due to the low process efficiencies, with metabolic processing ranking just below the fossil hydrogen reference case – another potentially competitive pathway.

Overall, this paper has found the following:

i. In our analysis, methane rich fuels have greater performance, due to the high gravimetric energy density and fewer processing stages than hydrogen, when used in SOFC.
ii. Hydrogen from natural gas and metabolic processing methods predominately has only slightly greater biomass feedstock demands. Light and dark fermentation have the highest, but can be combined for higher hydrogen yields, as well as metabolic processing, which could potentially reduce their high feedstock demand in future assessments.
iii. Anaerobic digestion and gasification have the highest process efficiencies, followed by SCWG. They have low to mid-range fuel gas and feedstock demands due to their high input/high yield processes.
iv. SCWG and Gasification syngas have the highest fuel gas demand and mid-range feedstock demands due to a low heating value.
v. The natural gas and fossil hydrogen reference cases are only presented for comparison and to demonstrate how competitive other pathways can be. Since they do not rely on any 'feedstock' a final comparison cannot truly be made. Nevertheless, it can be stated that the conversion efficiency (gas cleaning and reforming to hydrogen) do not differ from the biomass based pathways and the fossil carbon of the fuel will lead to considerable net carbon dioxide emissions. Biomass based fuels have no inherent net carbon emissions apart from the processing energy required, though this aspect is taken care of in the efficiency calculations.
vi. SOFC technologies outperformed PEFCs, with their internal reforming capabilities also allowing for a higher variation of fuel gases.

In addition to this assessment, it was found that each pathway feedstock determines the yield of fuel gases, and so high stack fuel demand may not be an issue if the biomass feedstock demand is low. Examples of this are the hydrogen pathways. They have low conversion process efficiency and fuel cell outputs, but moderate fuel gas and feedstock demands, due to the high gravimetric energy density of hydrogen, which increases the pathway's initial performance. This factor demonstrates the importance of looking at multiple perspectives in thoroughly assessing both the pathways and the technologies involved.

The performance of fermentation and metabolic processing pathways are a common theme across literature. Their low process efficiencies are due to the biological limitations, within the organisms themselves, for sunlight conversion. However, due to the purity of the hydrogen produced and high

Table 5 – Pathway summary table ranked in feedstock demand performance.

Ref.	Fuel Gas	Fuel Cell Type	Fuel Cell Output (kWh/kg)	Fuel Gas Demand (kg/MWh)	Raw Gas Demand (kg/MWh)	Raw Feedstock Demand (kg/MWh)	Raw Inputs and Waste Types
RCa	*De-sulphured Natural Gas*	SOFC	8.33	157.98	166.29	207.87	*Sour Natural Gas*[a]
1a	Biogas	SOFC	6.00	166.65	196.06	261.42	Biowastes[b]
1b	Biomethane	SOFC	8.33	119.99	200.72	267.62	Biowastes[b]
RCb	*(Fossil) Hydrogen*	SOFC	20.00	49.99	309.54	386.92	*Sour Natural Gas*[a]
RCb	*(Fossil) Hydrogen*	PEFC	15.00	66.66	412.76	515.95	*Sour Natural Gas*[a]
2	Hydrogen	SOFC	20.00	49.99	58.81	588.12	Algae starter, CO_2 & H_2O [c]
1c	Hydrogen (BM)	SOFC	20.00	49.99	491.89	655.86	Biowastes [b]
5a	Syngas	SOFC	2.17	461.50	542.94	775.63	Woody biomass [d]
2	Hydrogen	PEFC	15.00	66.66	78.43	784.25	Algae starter, CO_2 & H_2O [c]
1c	Hydrogen (BM)	PEFC	15.00	66.66	655.94	874.58	Biowastes [b]
4a	Syngas	SOFC	2.17	461.50	461.50	960.62	Woody biomass [d]
5b	Hydrogen (SG)	SOFC	20.00	49.99	789.76	1128.23	Woody biomass [d]
3a	Hydrogen	SOFC	20.00	49.99	58.81	1131.52	Biowastes [b]
4b	Hydrogen (SG)	SOFC	20.00	49.99	789.76	1397.30	Woody biomass [d]
5b	Hydrogen (SG)	PEFC	15.00	66.66	1053.14	1504.48	Woody biomass [d]
3a	Hydrogen	PEFC	15.00	66.66	78.43	1508.88	Biowastes [b]
3b	Hydrogen	SOFC	20.00	49.99	58.81	1851.58	Biowastes [b]
4b	Hydrogen (SG)	PEFC	15.00	66.66	1053.14	2192.11	Woody biomass [d]
3b	Hydrogen	PEFC	15.00	66.66	78.43	2469.07	Biowastes [b]

Reference guide:
1a Anaerobic Digestion, Biogas
1b Anaerobic Digestion, Biomethane from Biogas
1c Anaerobic Digestion, Hydrogen from Biomethane
2 Metabolic Processing, Hydrogen
3a Dark Fermentation, Hydrogen
3b Light Fermentation, Hydrogen
4a Gasification, Syngas
4b Gasification, Hydrogen from Syngas
5a Supercritical Water Gasification, Syngas
5b Supercritical Water Gasification, Hydrogen from Syngas
RCa Reference Case, Natural Gas
RCb Reference Case, Hydrogen from Natural Gas
[a] Sour natural gas, extracted from reserve.
[b] Agricultural residues and slurries.
[c] Agricultural wastewater is a suitable input for algae cultivation.
[d] Sustainable forestry residues, logging rejects, infested wood, etc.

hydrogen yields per dry cellular mass, the low efficiency of the fermentation processes does not out-weigh their potential. To improve metabolic processing, genetically engineered algae and bacteria would help the technology to become commercially viable. This would result in higher yields of hydrogen with a higher efficiency rate. These modifications at a cellular level could increase growth, speed up the uptake of glucose, sucrose *etc.*, and promote the continuous hydrogen production without inhibition [144,145]. Therefore, increasing the biological efficiency would significantly improve these biological pathways across all areas, as well as decrease the size (and therefore cost) of the bioreactors required to produce the same, if not higher, hydrogen yields.

Conclusions

Promising pathways for using biomass sources to derive gases for fuel cell applications in comparison with natural gas and fossil hydrogen were: anaerobic digestion and metabolic processing. These pathways can utilise waste residues, slurries, and wastewater from agricultural sectors to effectively produce useful gaseous fuels. Conversely, the results of the two reference cases are not specifically superior to the biomass pathways, showing that these are competitive systems. As natural gas and fossil hydrogen are based on fossil fuel sources, they do not constitute sustainable pathways. An additional finding was that the potential for fuel gas uses can vary due to the variation of biomass feedstock and fuel gas yields produced from these conversion pathways, including sources for both SOFCs and PEFCs.

Key findings of this study include the insight that even pathways with low efficiency and high fuel gas demands have the potential to be more sustainable. This is due to higher yielding biomass feedstock, compared to pathways with higher efficiency, low fuel gas demands, and higher feedstock demands. SOFCs proved to be a more favourable technology than PEFCs, due to their wide range of fuel choices and higher efficiency.

Declarations of interest

None.

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REFERENCES

[1] Basu P. Biomass gasification, pyrolysis and torrefaction: practical design and theory. London: Academic Press; 2013.
[2] REN21. Renewables Global status report. Paris: REN21 Secretariat; 2016.
[3] REN21. Renewables Global status report. Paris: REN21 Secretariat; 2015.
[4] Popp J, Lakner Z, Harangi-Rákos M, Fári M. The effect of bioenergy expansion: food, energy, and environment. Renew Sustain Energy Rev 2014;32:559–78.
[5] Balat H, Kırtay E. Hydrogen from biomass – present scenario and future prospects. Int J Hydrogen Energy 2010;35:7416–26.
[6] Ogden J, Steinbugler M, Kreutz T.Hydrogen as a fuel for fuel cell vehicles: a technical and economic comparison. Proceedings of: the 8th national hydrogen association meeting. Arlington, Virginia. 11-13 march 1997.
[7] National Energy Technology Laboratory. Syngas composition. 2016 [accessed January 2017], https://www.netl.doe.gov/research/coal/energy-systems/gasification/gasifipedia/syngas-composition.
[8] Reddy SN, Nanda S, Dalai AK, Kozinski JA. Supercritical water gasification of biomass for hydrogen production. Int J Hydrogen Energy 2014;39:6912–26.
[9] Rasi S. Biogas composition and upgrading to biomethane [Dissertation]. Finland: University of Jyväskylä; 2009.
[10] Rasi S, Veijanen A, Rintala J. Trace compounds of biogas from different biogas production plants. Energy 2007;32:1375–80.
[11] Biomass Technology Group. Supercritical water reforming. 2015. http://www.btgworld.com/en/rtd/technologies/supercritical-water-reforming [accessed October 2015].
[12] Chang ACC, Chang HF, Lin FJ, Lin KH, Chen CH. Biomass gasification for hydrogen production. Int J Hydrogen Energy 2011;36:14252–60.
[13] Styles D, Dominguez EM, Chadwick D. Environmental balance of the UK biogas sector: an evaluation by consequential life cycle assessment. Sci Total Environ 2016;560(561):241–53.
[14] Kariko-Buhwezi B, Mwesigue A, Arineitwe J, Colonna GP.Challenges to the sustainability of small scale biogas technologies in Uganda. Proceedings of: second international conference on advances in engineering and technology.
[15] Milne TA, Elam CC, Evans RJ. Hydrogen from biomass - state of the art and research challenges. Colorado: National Renewable Energy Laboratory; 2002.
[16] Balat M, Balat M. Political, economic and environmental impacts of biomass-based hydrogen. Int J Hydrogen Energy 2009;34:3589–603.
[17] Bičáková O, Straka P. Production of hydrogen from renewable resources and its effectiveness. Int J Hydrogen Energy 2012;37:11563–78.
[18] Braga LB, da Silva ME, Colombaroli TS, Tune CE, de Araujo FHM, Vane LF, et al. Chapter 2 - hydrogen production processes. In: Sustainable hydrogen production processes: energy, economic and ecological issues. Switzerland: Springer; 2016. p. 5–76.
[19] Das D, Veziroglu TN. Hydrogen production by biological processes: a survey of literature. Int J Hydrogen Energy 2001;26:13–28.
[20] Dincer I. Green methods for hydrogen production. Int J Hydrogen Energy 2012;37:1954–71.
[21] Dincer I, Acar C. Review and evaluation of hydrogen production methods for better sustainability. Int J Hydrogen Energy 2015;40:11094–111.
[22] Kalinci Y, Hepbasli A, Dincer I. Biomass-based hydrogen production: a review and analysis. Int J Hydrogen Energy 2009;34:8799–817.
[23] Levin DB, Chahine R. Challenges for renewable hydrogen production from biomass. Int J Hydrogen Energy 2010;35:4962–9.
[24] Manish S, Banerjee JR. Comparison of biohydrogen production processes. Int J Hydrogen Energy 2008;33:279–89.
[25] McKendry P. Energy production from biomass - part 1 - overview of biomass. Bioresour Technol 2002;83:37–46.
[26] McKendry P. Energy production from biomass (Part 2): conversion technologies. Bioresour Technol 2002;83:47–54.
[27] McPhail SJ, Cigolotti V, Moreno A. Fuel cells in the waste-to-energy chain. London: Springer-Verlag London; 2012.
[28] Ni M, Leung DYC, Leung MKH, Sumathy K. An overview of hydrogen production from biomass. Fuel Process Technol 2006;87:461–72.
[29] Sheffield JW, Sheffield C. Assessment of hydrogen energy for sustainable development. Netherlands: Springer; 2007.
[30] Alves HJ, Bley Junior C, Niklevicz RR, Frigo EP, Frigo MS, Coimbra-Araújo CH. Overview of hydrogen production technologies from biogas and the applications in fuel cells. Int J Hydrogen Energy 2013;38:5215–25.
[31] Claassen PAM, van Groenestijn JW, Janssen AJH, van Niel EWJ, Wijffels RH.Feasibility of biological hydrogen production from biomass for utilization in fuel cells. Proceedings of: the first World Conference on Biomass for Energy and Industry, vol vol. II. Sevilla, Spain. 5-9 June 2000.
[32] Voloshin RA, Rodionova MV, Zharmukhamedov SK, Nejat Veziroglu T, Allakhverdiev SI. Review: biofuel production from plant and algal biomass. Int J Hydrogen Energy 2016;41:17257–73.
[33] Dufour J, Serrano D, Galvez J, Moreno J, Garcia C. Life cycle assessment of processes for hydrogen production. Environmental feasibility and reduction of greenhouse gases emissions. Int J Hydrogen Energy 2009;34:1370–6.
[34] Dufour J, Serrano DP, Gálvez JL, González A, Soria E, Fierro JLG. Life cycle assessment of alternatives for hydrogen production from renewable and fossil sources. Int J Hydrogen Energy 2012;37:1173–83.
[35] Ghimire A, Frunzo L, Pirozzi F, Trably E, Escudie R, Lens PNL, et al. A review on dark fermentative biohydrogen production from organic biomass: process parameters and use of by-products. Appl Energy 2015;144:73–95.
[36] Ahmad AL, Yasin NHM, Derek CJC, Lim JK. Microalgae as a sustainable energy source for biodiesel production: a review. Renew Sustain Energy Rev 2011;15:584–93.
[37] Schlarb-Ridley B, Partker B. A UK roadmap for algal technologies - May 2013. Swindon: NERC-TSB Algal Bioenergy-SIG; 2013.
[38] Chau J, Sowlati T, Sokhansanj S, Preto F, Melin S, Bi X. Techno-economic analysis of wood biomass boilers for the greenhouse industry. Appl Energy 2009;86:364–71.
[39] Ahamed MS, Guo H, Taylor L, Tanino K. Heating demand and economic feasibility analysis for year-round vegetable

production in Canadian Prairies greenhouses. Inf Process Agric 2018.
[40] Chau J, Sowlati T, Sokhansanj S, Preto F, Melin S, Bi X. Economic sensitivity of wood biomass utilization for greenhouse heating application. Appl Energy 2009;86:616–21.
[41] Ericsson K, Werner S. The introduction and expansion of biomass use in Swedish district heating systems. Biomass Bioenergy 2016;94:57–65.
[42] Bibbiani C, Fantozzi F, Gargari C, Campiotti CA, Schettini E, Vox G. Wood biomass as sustainable energy for greenhouses heating in Italy. Agric Agric Sci Procedia 2016;8:637–45.
[43] Perea-Moreno A-J, Perea-Moreno M-Á, Hernandez-Escobedo Q, Manzano-Agugliaro F. Towards forest sustainability in Mediterranean countries using biomass as fuel for heating. J Clean Prod 2017;156:624–34.
[44] Las-Heras-Casas J, López-Ochoa LM, Paredes-Sánchez JP, López-González LM. Implementation of biomass boilers for heating and domestic hot water in multi-family buildings in Spain: energy, environmental, and economic assessment. J Clean Prod 2018;176:590–603.
[45] Badger P, Badger S, Puettmann ME, Steele P, Cooper J. Economic analysis of bio-oil. BioResources 2011;6:34–47.
[46] Li H, Chen Q, Zhang X, Finney KN, Sharifi VN, SwithenBank J. Evaluation of a biomass drying porcess using waste heat from process industries: a case study. Appl Therm Eng 2012;35:71–80.
[47] Abasaeed AE, Al-Fatesh AS, Naeem MA, Ibrahim AA, Fakeeha AH. Catalytic performance of CeO2 and ZrO2 supported Co catalysts for hydrogen production via dry reforming of methane. Int J Hydrogen Energy 2015;40:6818–26.
[48] Chou CT, Chen FH, Huang YJ, Yang HS. Carbon dioxide capture and hydrogen purification from synthesis gas by pressure swing absorption. Chem Eng Trans 2013;32:1855–60.
[49] Selivanovskaya SY, Zaripove SK, Latypova VZ, Hung YT. Treatment and disposal of biosolids. Environmental bioengineering, vol. 11. New York: Springer Science & Business Media; 2010. p. 1–52.
[50] Dahl R. A second life for scraps: making biogas from food waste. Environ Health Perspect 2015;123:A180–3.
[51] Wall G, Hammond B, Donlon D, Johnson ND, Smith JC. Commissioning and operation of high rate anaerobic lagoon (HARL) reactors. In: Proceedings of: 63rd annual water industry engineers and operators' conference. Warrnambool, Australia. 6-7 september; 2000.
[52] Kraemer T, Gamble S. Integrating anaerobic digestion with composting. Biocycle 2014;55(10):32.
[53] Wickie AC. Fixed-film anaerobic digestion of flushed manure. United states. 2004.
[54] Cherosky P, Li Y, Mancl K. Fact sheet AEX-653.1: manure to energy through anaerobic digestion. 2011. http://ati.ag.ohio-state.edu/factsheet/AEX-653.1 [accessed March 2017].
[55] Kim M, Ahn YH, Speece RE. Comparative process stability and efficiency of anaerobic digestion; mesophilic vs. thermophilic. Water Res 2002;36:4369–85.
[56] Dasgupta CN, Jose Gilbert J, Lindblad P, Heidorn T, Borgvang SA, Skjanes K, et al. Recent trends on the development of photobiological processes and photobioreactors for the improvement of hydrogen production. Int J Hydrogen Energy 2010;35:10218–38.
[57] Jorquera O, Kiperstok A, Sales EA, Embirucu M, Ghirardi ML. Comparative energy life-cycle analyses of microalgal biomass production in open ponds and photobioreactors. Bioresour Technol 2010;101:1406–13.
[58] Lam MK, Lee KT. Biohydrogen production from algae. 2013. p. 161–84.
[59] Xu L, Weathers PJ, Xiong XR, Liu CZ. Microalgal bioreactors: challenges and opportunities. Eng Life Sci 2009;9:178–89.
[60] Mata TM, Martins AA, Caetano NS. Microalgae for biodiesel production and other applications: a review. Renew Sustain Energy Rev 2010;14:217–32.
[61] Sierra E, Acién FG, Fernández JM, García JL, González C, Molina E. Characterization of a flat plate photobioreactor for the production of microalgae. Chem Eng J 2008;138:136–47.
[62] Ugwu CU, Aoyagi H, Uchiyama H. Photobioreactors for mass cultivation of algae. Bioresour Technol 2008;99:4021–8.
[63] Mahyudin AR, Furutani Y, Nakashimada Y, Kakizono T, Nishio N. Enhanced hydrogen production in altered mixed acid fermentation of glucose by Enterobacter aerogenes. J Ferment Bioeng 1997;83:358–63.
[64] Tanisho S, Kuromoto K, Kadokura N. Effect of Carbon Dioxide removal on hydrogen production by fermentation. Int J Hydrogen Energy 1998;23:559–63.
[65] Kim M, Baek J, Yun Y, Junsim S, Park S, Kim S. Hydrogen production from Chlamydomonas reinhardtii biomass using a two-step conversion process: anaerobic conversion and photosynthetic fermentation. Int J Hydrogen Energy 2006;31:812–6.
[66] Hussy I, Hawkes FR, Dinsdale R, Hawkes DL. Continuous fermentative hydrogen production from a wheat starch co-product by mixed microflora. Biotechnol Bioeng 2003;84:619–26.
[67] Kotay SM, Das D. Biohydrogen as a renewable energy resource—prospects and potentials. Int J Hydrogen Energy 2008;33:258–63.
[68] Gottardo M, Cavinato C, Bolzonella D, Pavan P. Dark fermentation optimization by anaerobic digestion sludge recirculation: effects on hydrogen production. Chem Eng Trans 2013;32:997–1002.
[69] Yokoyama S, Matasumura Y. 5.4. Hydrogen fermentation. In: The asian biomass handbook Japan. The Japan Institute of Energy; 2008. p. 132–4.
[70] Levin DB, Pitt L, Love M. Biohydrogen production: prospects and limitations to practical application. Int J Hydrogen Energy 2004;29:173–85.
[71] Chandra R, Nikhil GN, Mohan SV. Single-stage operation of hybrid dark-photo fermentation to enhance biohydrogen production through regulation of system redox condition: evaluation with real-field wastewater. Int J Mol Sci 2015;16:9540–56.
[72] Cardoso VL, Romão BB, Silva FTM, Santos JG, Batista FRX, Ferreira JS. Hydrogen production by dark fermentation. Chem Eng Trans 2014;38:2282–9216.
[73] Ostrem K. Greening waste: anaerobic digestion for treating the organic fraction of municipal solid wastes [MSc thesis]. Columbia: Columbia University; 2004.
[74] Verma S. Anaerobic digestion of biodegradable organics in municipal solid wastes [MSc thesis]. Columbia: Columbia University; 2002.
[75] Akhtar H, Sajjad S. LinkedIn presentation: biogas production from anaerobic digestion. 2014. https://www.slideshare.net/hameedakhtar155/presentation-of-em [accessed March 2017].
[76] RWTH Aachen University. Microbial conversion of biomass. 2008. https://www.ika.rwth-aachen.de/r2h/index.php/Microbial_conversion_of_biomass.html [accessed March 2017].
[77] Peters JW, Schut GJ, Boyd ES, Mulder DW, Shepard EM, Broderick JB, et al. [FeFe]- and [NiFe]-hydrogenase diversity, mechanism, and maturation. Biochim Biophys Acta 2015;1853:1350–69.

[78] Darensbourg MY, Lyon EJ, Zhao X, Georgakaki IP. The organometallic active site of [Fe]hydrogenase: models and entatic states. Proc Natl Acad Sci U S A 2003;100:3683–8.
[79] Kataoka N, Miya A, Kiriyama K. Studies on hydrogen production by continuous culture system of hydrogen-producing anaerobic bacteria. Water Sci Technol 1997;36:41–7.
[80] Djomo SN, Blumberga D. Comparative life cycle assessment of three biohydrogen pathways. Bioresour Technol 2011;102:2684–94.
[81] Ruoppolo G, Miccio F, Branchi P, Antonio P, Chirone R. Fluidized bed gasification of biomass and biomass/coal pellets in oxygen and steam atmosphere. Chem Eng Trans 2013;32:595–600.
[82] Koroneos C, Dompros A, Roumbas G. Hydrogen production via biomass gasification—a life cycle assessment approach. Chem Eng Process 2008;47:1261–8.
[83] Kumar A, Jones DD, Hanna MA. Thermochemical biomass gasification: a review of the current status of the technology. Energies 2009;2:556–81.
[84] Yakaboylu O, Harinck J, Smit K, de Jong W. Supercritical water gasification of biomass: a literature and technology overview. Energies 2015;8:859–94.
[85] Madenoğlu TG, Kurt S, Sağlam M, Yüksel M, Gökkaya D, Ballice L. Hydrogen production from some agricultural residues by catalytic subcritical and supercritical water gasification. J Supercrit Fluids 2012;67:22–8.
[86] Madenoğlu TG, Nikolaos B, Mehmet S, Mithat Y. Supercritical water gasification of real biomass feedstocks in continuous flow system. Int J Hydrogen Energy 2011;36:14408–15.
[87] Guo L, Lu Y, Zhang X, Ji C, Guan Y, Pei A. Hydrogen production by biomass gasification in supercritical water: a systematic experimental and analytical study. Catal Today 2007;129:275–86.
[88] Richards P, Fell M, Smith L, Keep M. Shale gas and fracking. Report ed. London: House of Commons Library; 2013.
[89] Spath PL, Mann MK. Life cycle assessment of hydrogen production via natural gas steam reforming. Colorado: National Renewable Energy Laboratory; 2001.
[90] Cetinkaya E, Dincer I, Naterer GF. Life cycle assessment of various hydrogen production methods. Int J Hydrogen Energy 2012;37:2071–80.
[91] Kalamaras CM, Efstathiou AM. Hydrogen production technologies: current state and future developments. Conf Pap Energy 2013;2013:1–9.
[92] Mascia PN, Scheffran J, Widholm JM. 1.6.2. Higher temperature processes. In: (eds) Biotechnology in agriculture and forestry - Volume 66: plant biotechnology for sustainable production of energy and Co-products. Heidelberg: Springer. p. 11-12.
[93] Krajnc N. Wood fuels handbook. Pristina:Food and Agricultural Organisation of the United Nations; 2015.
[94] Demirbas A. Chapter 2. Natural gas. In: Methane gas hydrate. London: Springer-Verlag; 2010. p. 57–76.
[95] Zhang JJ, Shen LP, Song H, Wang L, Wang XQ, Dong L. Research on adsorptive desulfurization of H2S from natural gas over MnxOy-CoxOy supported on activated carbon. Adsorpt Sci Technol 2016;34:134–43.
[96] Phyllis2. Database for biomass and biowaste. Energy Research Centre of the Netherlands; 2012.
[97] Steinberger-Wilckens R, Radcliffe J, Al-Mufachi NA, Dodds P, Abad AV, Jones O, et al. White paper: the role of hydrogen and fuel cells in delivering energy security for the UK. London: H2FC Supergen; 2017.
[98] Fuel Cell Technologies Office. Types of fuel cells. 2018. https://www.energy.gov/eere/fuelcells/types-fuel-cells [accessed September 2018].
[99] Kannan AM, Renugopalakrishnan V, Filipek S, Li P, Audette GF, Munukutla L. Bio-batteries and bio-fuel cells: leveraging on electronic charge transfer proteins. J Nanosci Nanotechnol 2008;8:1–13.
[100] Fuel Cells 2000. Types of fuel cells. 2016. http://hfcarchive.org/fuelcells/base.cgim?template=types_of_fuel_cells [accessed March 2016].
[101] Blomen LJMJ, Mugerwa MN. Fuel cell systems. New York: Springer Science & Business Media; 2013.
[102] Fuel Cells Technologies Office. Comparison of fuel cell technologies. Washington: US Department of Energy; 2016.
[103] Mat M, Liu X, Zhu Z, Zhu B. Development of cathodes for methanol and ethanol fuelled low temperature (300–600°C) solid oxide fuel cells. Int J Hydrogen Energy 2007;32:796–801.
[104] Chao C-C, Hsu C-M, Cui Y, Prinz FB. Improved solid oxide fuel cell performance with nanostructured electrolytes. ACS Nano 2011;5:5692–6.
[105] Stambouli AB, Traversa E. Solid oxide fuel cells (SOFCs): a review of an environmentally clean and efficient source of energy. Renew Sustain Energy Rev 2002;6:433–55.
[106] Dodds PE, Staffell I, Hawkes AD, Li F, Grünewald P, McDowall W, et al. Hydrogen and fuel cell technologies for heating: a review. Int J Hydrogen Energy 2015;40:2065–83.
[107] Tesfai A. Small and mighty – the performance of a fuel cell micro-CHP. CIBSE J 2015:74–8. November 2015.
[108] Agnolucci P. Prospects of fuel cell auxiliary power units in the civil markets. Int J Hydrogen Energy 2007;32:4306–18.
[109] Veziroglu A, Macario R. Fuel cell vehicles: state of the art with economic and environmental concerns. Int J Hydrogen Energy 2011;36:25–43.
[110] Corbo P, Migliardini F, Veneri O. Dynamic behaviour of hydrogen fuel cells for automotive application. Renew Energy 2009;34:1955–61.
[111] Wee J. Applications of proton exchange membrane fuel cells systems. Renew Sustain Energy Rev 2007;11:1720–38.
[112] Lokurlu A. Fuel cells for mobile and stationary applications—cost analysis for combined heat and power stations on the basis of fuel cells. Int J Hydrogen Energy 2003;28:703–11.
[113] Nugent P, Belmabkhout Y, Burd SD, Cairns AJ, Luebke R, Forrest K, et al. Porous materials with optimal adsorption thermodynamics and kinetics for CO2 separation. Nature 2013;495:80–4.
[114] Srirangan K, Akawi L, Moo-Young M, Chou CP. Towards sustainable production of clean energy carriers from biomass resources. Appl Energy 2012;100:172–86.
[115] Wang M, Lawal A, Stephenson P, Sidders J, Ramshaw C. Post-combustion CO2 capture with chemical absorption: a state-of-the-art review. Chem Eng Res Des 2011;89:1609–24.
[116] Grande CA. Advances in pressure swing adsorption for gas separation. ISRN Chem Eng 2012;2012:1–13.
[117] Membrane and Technology Research Ltd. Membrane solutions for industrial seperations. 2016. http://www.mtrinc.com/index.html [accessed February 2017].
[118] Shimeskit B, Mukhtar H. Natural gas purification technologies – major advances for CO2 separation and future directions. In: Advances in natural gas technology. Croatia: InTech; 2012. p. 235–70.
[119] Lee JW. Advanced biofuels and bioproducts. New York: Springer Science & Business Media; 2012.
[120] Charles W, Carnaje NP, Cord-Ruwisch R. Methane conversion efficiency as a simple control parameter for an anaerobic digester at high loading rates. Water Sci Technol 2011;64:534–9.
[121] Rodrigues R, Marcilio NR, Trierweiler JO, Godinho M. Thermodynamic efficiency analysis of gasification of high

ash coal and biomass. In: Proceedings of: international conference on coal science and technology. Ovidedo. 9-13 october; 2011.
[122] Hanif MU, Capareda SC, Iqbal H, Arazo RO, Baig MA. Effects of pyrolysis temperature on product yields and energy recovery from Co-feeding of cotton gin trash, cow manure, and microalgae: a simulation study. PloS One 2016;11:e0152230.
[123] Chakrabarti HC. Biomass gasification - basics and considerations. India: Dankuni Coal Complex; 2013.
[124] Gassner M, Vogel F, Heyen G, Maréchal F. Optimal process design for the polygeneration of SNG, power and heat by hydrothermal gasification of waste biomass: thermo-economic process modelling and integration. Energy Environ Sci 2011;4:1726.
[125] Boukis N, Galla U, Diem V, D'Jesus P, Dinjus E. Hydrogen generation from wet biomass in supercritical water. In: Proceedings of: 2nd world conference on biomass for energy, industry and climate protection. Rome, Italy. 10-14 May; 2004.
[126] Sørensen B. Comparison between hydrogen fuel cell vehicles and bio-diesel vehicles. In: 16th world hydrogen energy conference, Lyon, France: paper S24-111. Sevanova: IHEA CDROM #111; 2006. p. 1–11.
[127] Carbo MC, Jansen D, Boon J, Dijkstra JW, van den Brink RW, Verkooijen AHM. Staged water-gas shift configuration: key to efficiency penalty reduction during pre-combustion decarbonisation in IGCC. Energy Procedia 2009;1:661–8.
[128] Haryanto A, Fernando SD, Filip To SD, Steele PH, Pordesimo L, Adhikari S. Hydrogen production through the Water–Gas shift reaction: thermodynamic equilibrium versus experimental results over supported Ni catalysts. Energy Fuels 2009;23:3097–102.
[129] Liu PKT. II.D.2 water-gas shift reaction via a single-stage low-temperature membrane reactor. Pittsborough: Department of Energy; 2007.
[130] Benemann JR. Feasibility analysis of photobiological hydrogen production. Int J Hydrogen Energy 1997;22:979–87.
[131] Neumann P, von Linde F. Special Equipment: options for economical supply of hydrogen. Munich, Germany: Caloric Anlagenbau GmbH; 2003.
[132] James BD, Baum GN, Perez J, Baum KN. Technoeconomic boundary analysis of biological pathways to hydrogen production. Golden, CO: NREL; 2009.
[133] Hyne NR. In: Dictionary of petroleum exploration, drilling & production. 2nd ed. Tusla, Oklahoma: PennWell Corporation; 2014. p. 417–48.
[134] Huertas JI, Giraldo N, Izquierdo S. 7. Removal of H2S and CO2 from biogas by amine absorption. In: Mass transfer in chemical engineering processes. Croatia. InTech Europe; 2011. p. 133–50.
[135] Keachagiopoulos PN, Voutetakis SS, Lemonidou AA, Vasalos IA. Hydrogen production via steam reforming of the aqueous phase of bio-oil in a fixed bed reactor. Energy Fuels 2006;20:2155–63.
[136] Yokoyama S, Matasumura Y. 4.6. Hydrothermal liquefaction. In: The asian biomass handbook. Japan: The Japan Institute of Energy; 2008. p. 114–6.
[137] Convert units. Measurement unit converter. 2017. http://www.convertunits.com [accessed April 2017].
[138] Jorgensen PJ. PlanEnergi, researcher for a day. Biogas - green energy. Denmark: Aarhus University; 2009.
[139] Smil V. 1.1 methane's advantages and drawbacks. In: Natural gas: fuel for the 21st century. John Wiley & Sons; 2015. p. 4–12.
[140] Pant KK, Gupta RB. Chapter 1. Fundamentals and use of hydrogen as a fuel. In: Hydrogen fuel: production, transport and storage. CRC Press; 2008. p. 2–32.
[141] Mustafa A, Calay RK, Mustafa MY. A techno-economic study of a biomass gasification plant for the production of transport biofuel for small communities. Energy Procedia 2017;112:529–36.
[142] Eswara AK, Misra SC, Ramesh US. Introduction to natural gas: a comparative study of its storage, fuel costs and emissions for a harbor tug. In: Proceedings of: annual meeting of society of naval architects & marine engineers. Washington, USA; 8th November 2013.
[143] Hopwood L. Farm-scale Anaerobic digestion plant efficiency. York: NNFCC; 2011.
[144] Kruse O, Hankamer B. Microalgal hydrogen production. Curr Opin Biotechnol 2010;21:238–43.
[145] Mathews J, Wang G. Metabolic pathway engineering for enhanced biohydrogen production. Int J Hydrogen Energy 2009;34:7404–16.